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DETERMINATION OF THE HOMOGENEITY RANGE OF La_2CuO_4

by

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Determination of the Homogeneity Range of La_2CuO_4

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Pure La_2CuO_4 was prepared by decomposition of the nitrates followed by an oxygen anneal at 500°C and 600 psi of oxygen. The extent of anion vacancies was studied by thermogravimetric analysis, x-ray diffraction and magnetic susceptibility. The magnitude of this deficiency is less than can be unambiguously ascertained by direct thermogravimetric analysis which has a limit in accuracy in x of .01 for the composition $\text{La}_2\text{CuO}_{4-x}$. However, significant shifts in the Néel temperatures confirmed the variation in anion vacancy concentrations. Attempts to modify the cation ratio of $\text{La}:\text{Cu} = 2:1$ failed to yield single phase material.

La_2CuO_4 was reported by Longo and Raccah (1) to show an orthorhombic distortion of the K_2NiF_4 structure with $a = 5.363\text{\AA}$, $b = 5.409\text{\AA}$ and $c = 13.17\text{\AA}$. It was also reported (2,3) that La_2CuO_4 has a variable concentration of anion vacancies which may be represented as $\text{La}_2\text{CuO}_{4-x}$. The value of x is dependent on the method of preparation.

$\text{La}_2\text{CuO}_{4-x}$ undergoes a second order tetragonal-orthorhombic phase transformation and the temperature at which this transformation occurs is dependent on the value of x (2). A plot of the transformation temperature vs anion defect concentration in $\text{La}_2\text{CuO}_{4-x}$ indicates that for a change of .03 in the value of x , the transition temperature is increased by $\sim 75\text{ K}$. A magnetic susceptibility anomaly also occurs which is due to long-range antiferromagnetic ordering in the sample (3, 4). It was also shown that the Néel temperature is sensitive to the oxygen vacancy concentration and increases as the anion vacancies are increased.

There appear still to be some uncertainties concerning the magnetic properties of $\text{La}_2\text{CuO}_{4-x}$ as x approaches zero. Whereas there is agreement concerning the observed increase in T_N as the anion vacancy concentration is increased, the disappearance of observable antiferromagnetic behavior in some of the samples prepared (2,5,6) has been difficult to reproduce.



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Experimental

In this study samples were prepared which contained controlled concentrations of both anion and cation vacancies. All samples were prepared by dissolving copper (5-9's Aesar Chemical Co.) and La_2O_3 (4-9's Aesar Chemical Co.) in 1:1 dilute nitric acid. The solution was evaporated on a hot plate to dryness, then placed in a furnace, and heated to 500°C for 24 hours in order to decompose the nitrates. The product was ground and reheated to 800°C for 24 hours. After a final grinding the product was heated for 24 hours at 950°C and allowed to slow cool in air to room temperature. For the sample corresponding to $\text{La}_2\text{CuO}_{4.00(1)}$ the product was annealed for 12 hours at 500°C and 600 psi of oxygen. In order to prepare samples deficient in oxygen the products were heated in a predried, pure argon atmosphere (flow rate = 50 sccm/min) from 500 - 800°C . All samples were analyzed by reduction in a H_2/Ar (15/85) atmosphere to copper metal and lanthanum oxide.

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Characterization of Products

Powder diffraction patterns were obtained with a Philips-Norelco diffractometer using monochromatic high-intensity $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5405\text{\AA}$). For qualitative identification of the phases present, the patterns were taken from $12^\circ < 2\theta < 72^\circ$ with a scan rate of $1^\circ 2\theta/\text{min}$ and a chart speed of 30 in/hr. The scan rate used to obtain x-ray patterns for precision cell constant determination was $0.25^\circ 2\theta/\text{min}$ with a chart speed of 30 in/hr. Cell parameters were determined by a least-squares refinement of the reflections using a computer program which corrects for the systematic errors of the measurement.

Temperature programmed reductions of all samples were carried out using a Cahn System 113 thermal balance. Each sample was purged at room temperature in a stream of H_2/Ar (15/85) for 2 hours. Then the temperature was increased to 1000°C at a rate of $60^\circ/\text{hr}$. The flow rate of the gas mixture was 60 sccm/min.

Magnetic susceptibility measurements were carried out using a Faraday Balance from 77 to 300 K with a field strength of 10.4 kOe. Honda-Owen (field dependency) measurements were carried out at 77 and 300 K.

Results and Discussion

X-ray diffraction data of the various phases prepared and analyzed are compared in Table I with those reported by previous investigators (1,5,6). It can be seen that the best agreement is with the parameters reported by Longo and Raccach (1) and the greatest discrepancy is with those of Saez Puche et al. (6). Thermogravimetric analysis of the pure samples resulted in a composition determined by weight loss on reductions to $\text{La}_2\text{O}_3 + \text{Cu}$ to be $\text{La}_2\text{CuO}_{4.00(1)}$. In order to establish the range of homogeneity of the phase La_2CuO_4 , varying ratios of lanthanum to copper were reacted where $\text{La}:\text{Cu} = 2.05:1$ to $1.90:1$. The samples were prepared precisely according to the method used for La_2CuO_4 and the results are given in Table II. It can readily be seen that the pure

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Table I. Cell Parameters Reported for "Pure" La_2CuO_4

Composition	T_N	Cell Constants (Abma orientation)			Ref.
		a	b	c	
La_2CuO_4	--	5.363	5.409	13.17	(1)
La_2CuO_4	--	5.366	5.402	13.15	(5)
La_2CuO_4	--	5.342	5.434	13.16	(6)
$\text{La}_2\text{CuO}_{4.00(1)}$	240	5.358	5.400	13.16	This work

compound exists over an extremely narrow range of composition with respect to the La:Cu ratios. For the sample with nominal composition, La:Cu = 1.95:1, x-ray diffraction patterns indicated the presence of a single phase even at the maximum sensitivity of the Philips instrument used. However, counts for 400 seconds were made over the range $38.5 \leq 2\theta \leq 39.5^\circ$. The (111) peak of Cu occurred at 38.9° . From these measurements the presence of CuO could barely be detected (Figure 1).

Table II. Product Phases Observed for Various Cation Ratios

Nominal	Composition		Phases Identified by X-ray Analysis
La	:	Cu	
2.05	:	1	$\text{La}_2\text{CuO}_4 + \text{La}_2\text{O}_3$
2.00	:	1	La_2CuO_4
1.95	:	1	La_2CuO_4 (step counting showed trace of CuO)
1.90	:	1	$\text{La}_2\text{CuO}_4 + \text{CuO}$

The samples prepared by double decomposition of the nitrates followed by an anneal at 500°C and 600 psi oxygen resulted in maximum oxygen content as determined by thermogravimetric analysis. Table III compares the above compound with those annealed in an argon or argon/air atmosphere at 500°C and 800°C . Samples heated in argon between 500 and 800°C were single phase as indicated by x-ray analysis and showed no measurable difference in cell constants.

Table III. Variation of Cell Parameters and Magnetic Properties with Type of Anneal for La_2CuO_4

Analyzed Composition or Preparative Condition	T_N	χ (emu/mol)	Cell Constants		
			a	b	c
$\text{La}_2\text{CuO}_{4.00(1)}$					
500°C , 600 psi O_2	240	9×10^{-5}	5.358(2)	5.400(2)	13.16(1)
500°C Ar/Air 80/20	260	13×10^{-5}	5.358(2)	5.405(2)	13.15(1)
500°C Ar	300	13×10^{-5}	5.355(2)	5.406(2)	13.14(1)
800°C Ar	300	13×10^{-5}	5.356(2)	5.408(2)	13.15(1)

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However, at 900°C there was decomposition of the products as indicated by the appearance of a strong lanthanum oxide peak in the x-ray diffraction pattern. As can be seen from Table III and Figure 2, the Néel point (which is chosen as the maximum in the plot of X vs T) shifts from 240 K for $\text{La}_2\text{CuO}_{4.00(1)}$ to 300 K for a composition containing a small oxygen deficiency. The magnitude of this deficiency is less than can be unambiguously ascertained by direct thermogravimetric analysis which has a limit in accuracy of ± 0.01 . Furthermore, changes in cell parameters are capable only of differentiating between pure $\text{La}_2\text{CuO}_{4.00(1)}$ with $T_N = 240$ K and the oxygen deficient composition with a T_N of 300 K.

It was shown by Mitsuda et al (3) that in the system $\text{La}_2\text{CuO}_{4-x}$ the Néel temperature is exceedingly sensitive to the oxygen vacancy concentration. Samples of pure La_2CuO_4 have been reported to show no antiferromagnetic ordering down to 4.2 K (2,5,7). However, despite all efforts to reproduce the procedures indicated by these authors, no sample could be synthesized in this laboratory that did not show a T_N . It can be seen from Figure 2 that the removal of a small amount of oxygen shifts T_N from ~ 240 to 300 K. This agrees with the work of Uemura et al. (8) in which two samples were prepared at 950°C in air and one of them was heated at 260 psi of O_2 at 500°C. Samples of $\text{La}_2\text{CuO}_{4.00(1)}$ prepared in this laboratory at 500°C up to 2000 psi of O_2 still showed a Neel temperature of 240 K. The shift in the Néel temperature of a sample slightly deficient in oxygen is consistent with the observation by Kasowski et al. (9) that oxygen vacancies occur in the Cu-O plane. Such vacancies could result in the strengthening of the antiferromagnetic interactions between Cu-O-Cu planes along the c-direction in the structure.

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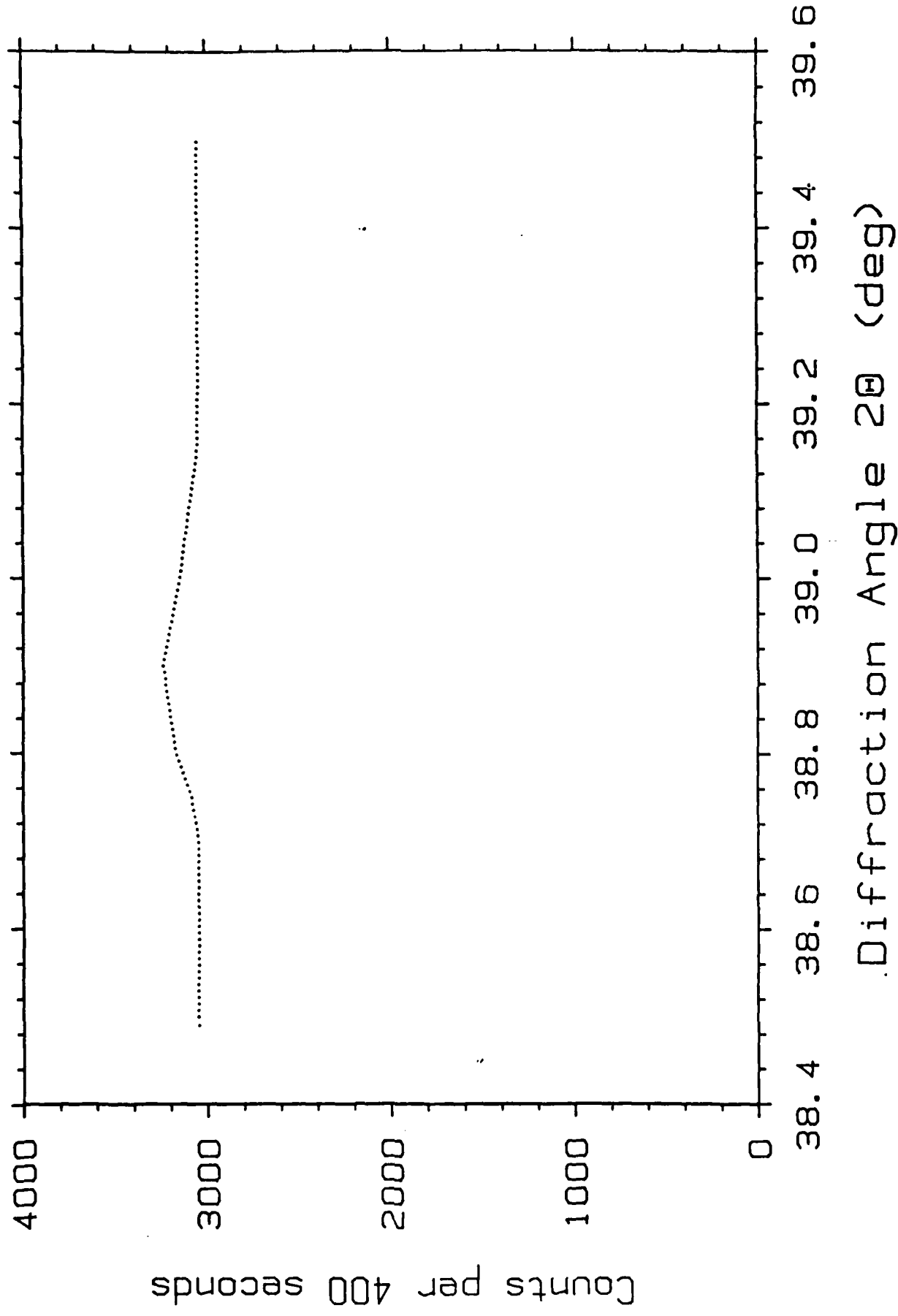
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Step Counts for $\text{La}_{1.95}\text{CuO}_{3.925}$



La_2CuO_4 after Anneal

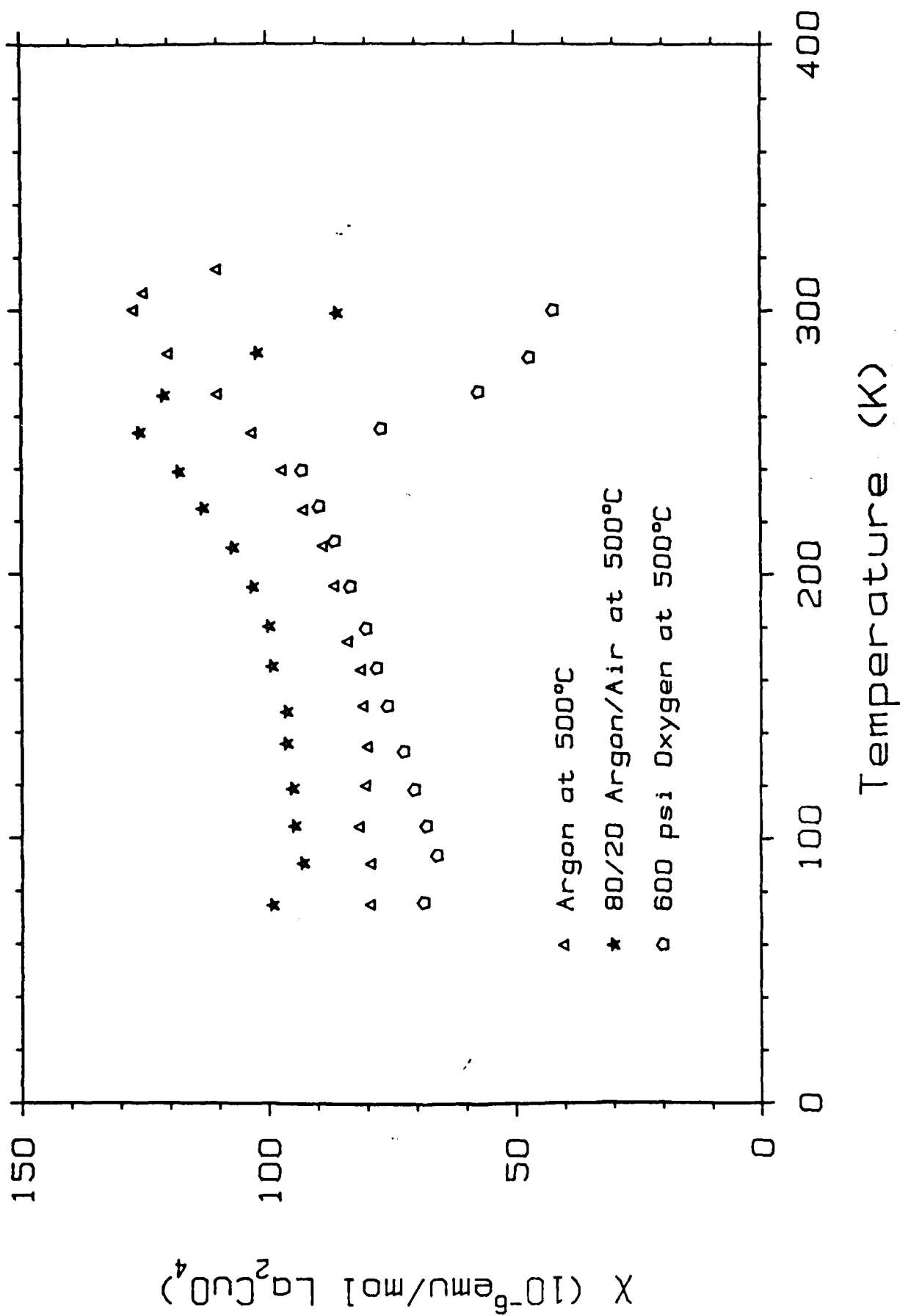


Figure 1. X-ray step counts for the nominal sample of $\text{La}_{1.95}\text{CuO}_{3.925}$, showing the strongest peak of CuO .

Figure 2. Magnetic susceptibility as a function of temperature for samples of La_2CuO_4 annealed at 500°C in 600 psi of oxygen, in an 80/20 argon/air mixture, and in pure argon.